



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : C09D 195/00	A1	(11) International Publication Number: WO 00/68329 (43) International Publication Date: 16 November 2000 (16.11.00)
(21) International Application Number: PCT/US00/12568 (22) International Filing Date: 8 May 2000 (08.05.00) (30) Priority Data: 09/309,653 10 May 1999 (10.05.99) US (71) Applicant: GOLDSCHMIDT CHEMICAL COMPANY [US/US]; 914 East Randolph Road, P.O. Box 1299, Hopewell, VA 23860 (US). (72) Inventors: CHATTERJEE, Roger; 1909 Royal Oak Drive, Lewis Center, OH 43035 (US). MILBURN, Charles, R.; 255 N. Franklin Street, Delaware, OH 43035 (US). (74) Agents: DIGIGLIO, Frank, S. et al.; Scully, Scott, Murphy & Presser, 400 Garden City Plaza, Garden City, NY 11530 (US).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  Published With international search report.	

(54) Title: ROAD REPAIR METHODS AND FAST BREAKING ASPHALT EMULSION COMPOSITIONS USEFUL THEREWITH

## (57) Abstract

Road repair methods which involve application of an aggregate-free rapid setting aqueous asphalt residue emulsion onto a road surface, followed by application of aggregate to the applied emulsion. The emulsion comprises a fatty acid/ethylenepolyamine emulsifier. These faster breaking asphalt emulsion compositions are also potentially useful for roofing and coating applications.

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

ROAD REPAIR METHODS AND FAST BREAKING ASPHALT EMULSION  
COMPOSITIONS USEFUL THEREWITH

5           This invention relates to new and useful  
asphalt emulsions used for spray applied road  
construction or repair applications and to non-paving  
applications such as roof and asphaltic coatings.

10           In road repair the use of asphalt emulsions in  
a variety of applications has become increasingly  
important. Examples include "tack coat," "cold mix,"  
"fog seal," "chip seal," and "slurry seal," or  
"microsurfacing.." Tack coat is a spray emulsion applied  
to the existing surface to improve adhesion with the new  
paving. Cold mix is emulsion mixed with aggregate for  
15 pothole patching or moderately thick paving up to two  
inches thick. Fog seal is a cosmetic spray applied to  
the finished pavement. Chip seal is a spray emulsion  
that is then covered with a thin layer of stones. Slurry  
seal and microsurfacing are mixtures of emulsion and a  
20 complex mixed aggregate which is applied on top of old  
pavement.

          These emulsions can be cationic, anionic or  
non-ionic depending upon the emulsifier. A critical  
emulsion characteristic is the amount of time from when  
5 the emulsion is mixed with or contacts the aggregate  
until the asphalt and water in the emulsion separate  
which causes the asphalt to set giving a firm water  
resistant coating which holds the aggregate together and  
adheres it to the old pavement. The set times are  
0 normally categorized as quick set, rapid set, medium set  
and slow set. ASTM standards have been promulgated for  
standardized emulsions within these set time categories

which are commonly used for contracting specifications  
(See ASTM D 2397).

5       Microsurfacing and slurry seal systems use a  
cationic or anionic asphalt emulsion in water, which is  
mixed at the work site with an aggregate containing a  
high quantity of fines or dusty material. For such  
applications at least 25%, and sometimes as much as 90%  
of the aggregate will pass through a 16 mesh screen  
(USS). Within a short time after contacting the  
10       aggregate, the emulsion breaks and the asphalt/aggregate  
separates from the water phase. Before the emulsion  
breaks or sets, the mixture is applied to the road  
surface and leveled. Microsurfacing systems tend to be  
polymer modified and can be applied in relatively thick  
15       layers, as they are commonly used for rut filling. Slurry  
seal systems are typically applied in layers only as  
thick as the largest stone in the composition. Amidoamine  
and imidazoline and their associated quaternary  
emulsifiers have been described as cationic emulsifiers  
20       for such microsurfacing and/or slurry seal applications  
as have polyamines such as alkyl aminopolypropylamines  
and other more complex surfactants. However, as breaking  
of a cationic emulsion is usually triggered by the  
contact with stone or other aggregate material, much work  
5       has been done investigating cationic emulsifiers which  
provide longer breaking times so that the mixture does  
not set up in the mixing equipment before the slurry can  
be applied to the road surface. To extend the stability  
of the emulsion during mixing the typical emulsifier use  
0       levels for microsurfacing or slurry seal emulsions are  
quite high ranging from 0.75% to 1.5% by weight of the  
final emulsion. Documents describing such work include  
US Patent Nos. 5,242,492; 5,273,683; 4,462,840; and  
5,429,695.

Other references describing emulsifiers for cationic emulsions include US Patent Nos. 4,172,046; 4,579,593; and 4,724,245.

5 An application in which a bitumen asphalt emulsion is sprayed onto a road surface where it rapidly coalesces is described in US Patent Nos. 5,474,607 and 5,518,538. According to these references a more rapid coalescence is obtained by creating a bimodal particle size in the emulsion or by adding chemical agents which  
10 raise the pH of the emulsion.

Another road maintenance method is known as a "chip seal". In a chip seal application, an asphalt emulsion is sprayed on to the road surface and then clean, frequently washed, narrow size range, stone  
5 aggregate, typically about 1/4 inch (6.4 mm) and containing little fines material passing thru 200 mesh, is spread on top of the sprayed emulsion. Aggregate sizes used for various types of chip seal contain essentially no material passing 16 mesh, and may go as  
0 high as 3/4 inch mesh, or even higher, with each application typically using a narrow fractional size range within these parameters. As with slurry seal, the chip seal application is only one stone thick, but in the chip seal technique the aggregate is not mixed with the  
5 asphalt emulsion before being applied to the road. The repair is typically finished with light tire roller compaction. Because the aggregate is clean, and has very little material less than #16 mesh and is not mixed with the emulsion prior to application onto the road,  
1 much lower emulsifier levels are used, typically 0.17 to 0.30% by weight of the final emulsion. The asphalt penetrates and seals the road bed and adheres the aggregate to the existing asphalt surface and the stone restores the road surface. Although very cost effective,

chip seal road repair is done predominantly on secondary roads because there is a propensity of loose uncoated chips to damage cars and trucks on more heavily used high speed roads such as freeways.

5           Conventional cationic emulsions occasionally created a localized environmental problem in chip seal applications, for instance if a sudden thunderstorm overtakes the job site and washes unbroken emulsion into the ditch or storm sewer system. This potential problem  
10 can hinder the use of chip seal repair techniques, especially in areas of frequent rainfall during road repair seasons. This situation tends to be even worse in the spring or fall or in cooler regions as lower temperatures cause emulsions to set more slowly.  
15 Obviously as the unbroken emulsion is washed off the durability and quality of the asphalt repair is reduced. Thus there is a need for a faster setting asphalt emulsion.

20           An especially difficult test for chip seal emulsion formulations, designated VIM-65, has been developed by the State of Virginia. According to this test, a rapid setting emulsion, such as an ASTM D 2397 CRS-2 emulsion, is mixed with stones at a rate of 30 g emulsion and 200 grams of prewetted and towel dried  
25 stones for a maximum of 30 seconds, followed by an immediate washing with sprinkled water (using quart can with 18 holes of 0.125 inch dia), until clear water is obtained or 3/4 of can has been emptied. To pass the test, 100% coverage of the stones with a tacky asphalt  
0 coating must be observed. Conventional cationic rapid setting asphalt emulsion formulations typically provide only 60-75% coating under this test. Remembering that an essential difference between chip seal and slurry seal/microsurfacing is that in chip seal application the

emulsion is not mixed with the aggregate prior to application to the road surface, this VIM-65 test includes mixing simply to insure reproducible exposure of the stone surfaces to the emulsion and to defined a fixed period of time for the emulsion to set.

A proprietary formulation capable of passing this test has reportedly been developed by some suppliers, but that formulation is said to be highly unstable, with a safe storage time of only a few days or less. The practice of adding a destabilizing agent to an asphalt emulsion is known but is extremely risky and unacceptable. One of the critical specifications for emulsions is the 'sieve test' which measures the amount of deemulsified asphalt that is captured on a #20 USS mesh screen after the emulsion has been stored, typically for a 7 day period. If more than 0.1% is captured in the screen the emulsion fails the test and should not be used for spray applications because it can plug or partially plug the spray nozzles which will cause uneven emulsion application to the road surface and subsequent failure. Additionally, the emulsions are frequently stored in tanks of 50,000 gallons (189,000 L) or more. If the emulsion breaks in such a large tank, the resulting mixture of water and asphalt is very difficult to separate and reprocess. The asphalt is frequently not pumpable until heated above the boiling point of water thus potentially creating steam in a dangerous situation.

Even though there are some similarities between chip seal and slurry seal applications, there are very few emulsifiers developed for one application which are used extensively in the other application. The fundamental reason is that the aggregate used in slurry seal contains a large amount of material passing through #16 Mesh which, due to its high specific surface area,

reacts very strongly with the emulsifying surfactant. In contrast, the aggregate used in chip seal is much larger, has a smaller specific surface area, and thus reacts to a lesser extent. This is compensated for to some extent by the fact that the surfactant use levels are much higher for slurry seal than for chip seal. But even so, if emulsions made with most chip seal emulsifiers were used in slurry seal/microsurfacing they would most likely break prematurely causing the slurry seal mixture to become hard and unflowable in the mixing equipment, or to become too stiff to spread in an even thin layer on the old pavement and adhere well to the old pavement. Similarly most emulsions made with slurry seal emulsifiers at chip seal levels of surfactant will break much too slowly when clean, washed essentially single sized and much larger chips are spread on top of the emulsion sprayed onto the old pavement.

Therefore a need exists for improved cationic asphalt emulsions adapted for chip seal applications which are stable in shipping and storage but which break faster than conventional emulsions. In the case of the State of Virginia this faster breaking characteristic is evidenced by more complete coating in their test method. Extension of chip seal techniques to primary roads and city streets may also be possible if fast breaking emulsion formulations were available which gave better stone coverage and adhesion. Also emulsions exhibiting these behaviors are considered to have similar benefit in industrial coating applications as well as tar and gravel roofing applications.

It has now been discovered that amidoamines or imidazoline emulsifiers prepared from fatty acids or their esters, and ethylenepolyamines, can be employed effectively as emulsifiers for sprayed emulsion



applications, and further that, within narrow use ranges, such emulsifiers may be used to prepare stable asphalt emulsions useful for the most demanding chip seal applications. In particular, as evidence of the faster breaking, faster setting emulsion properties obtainable, coating percentages in excess of 90% can be readily obtained under the rigorous VIM-65 test, described above, and preferred compositions can be formulated which fully meet the 100% coating requirement under this test.

The emulsions prepared in this manner have little tendency to break in the storage tank under conventional storage conditions for cationic rapid set emulsions. Under the conditions of the sieve test, described above, not more than 0.1% of the emulsion will be retained on a 20 mesh USS screen after a storage period of 7 days.

In one aspect, the invention is a surface repair or finishing method comprising: (a) applying an aqueous asphalt residue emulsion onto a substrate surface; (b) applying stone aggregate to the emulsion after the emulsion has been applied to the surface, wherein the stone aggregate comprises no more than 10% by weight of material of less than 16 mesh USS size, and the emulsion comprises a fatty acid/ethylenepolyamine emulsifier characterized by at least one fatty acid residue and an ethylenepolyamine residue, the fatty acid residue(s) and the ethylenepolyamine residue together forming an amidoamine compound or an imidazoline compound or a mixture thereof.

The method is particularly useful for chip seal road repair applications. However, it may also be advantageously employed in flat roof installation and repair applications, where ambient temperature

application allows for reduced production volatiles and less hazard to workers compared to conventional hot tar roofing techniques.

5 A further aspect of the invention is a surface repair or finishing method comprising spray applying an aqueous asphalt residue emulsion onto a substrate surface, wherein the emulsion comprises an asphalt residue content of at least 60%, and a fatty acid/ethylenepolyamine emulsifier characterized by at least one fatty acid residue and an ethylenepolyamine residue, the fatty acid residue(s) and the ethylenepolyamine residue together forming an amidoamine compound or an imidazoline compound or a mixture thereof. In addition to the chip seal and roofing applications described above, spray application of such emulsions can be used to provide asphalt coatings on concrete substrates such as concrete pipe and on other substrates such as automobile underbodies. For these latter applications, too, spray application of a rapid setting storage stable emulsion provides reduced environmental and safety hazards compared to spraying hot tar.

A further application is an aqueous asphalt emulsion composition. The emulsion comprises, on a composition weight basis:

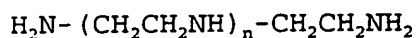
5 65-80%, preferably 68-75%, by weight of the emulsion of asphalt residue; and

0.10-0.5% of a fatty acid/ethylenepolyamine emulsifier characterized by at least one fatty acid residue and an ethylenepolyamine residue, the fatty acid residue(s) and the ethylenepolyamine residue together forming an amidoamine compound or an imidazoline compound or a mixture thereof.

Other features of the invention are described in the following description of the preferred embodiments.

The emulsion is suitably prepared using a conventional asphalt residue material for the specific application contemplated for the emulsion. For chip seal road repair, AC5-AC20 asphalts, blends thereof, and equivalents of such asphalts are preferred, more preferably AC10 asphalt or equivalent. It is generally preferred that the emulsion contain at least 65% by weight of the asphalt residue content, more preferably at least 68% by weight. Generally the maximum asphalt residue load which may be practically formulated for spray applications will be about 80% by weight or less, more typically about 75%. For some pour and spread application techniques somewhat higher asphalt residue loading may be practical.

The amidoamine or imidazoline emulsifiers of the invention are suitably prepared from fatty acids or their esters, and ethylenepolyamines. As used herein "ethylenepolyamines" includes ethyleneadiamine and ethylenediamine oligomers of the formula:



where n is 1-10, preferably 1-5. Suitable ethylenepolyamines include, in addition to ethylenediamine, diethylenetriamine (DETA), triethylenetetraamine (TETA) and tetraethylenepentaamine (TEPA), etc. The terms "amidoamine" and "imidazoline", as used herein, should be understood to encompass the mono and di fatty acid adducts of such ethylenepolyamines. Preferred such emulsifiers are fatty acid amidoamines and imidazolines based on diethylenetriamine (FA-DETA).

To prepare the FA-DETA emulsifier, fatty acid may be reacted in known manner with diethylenetriamine to produce an amidoamine or imidazoline. It is also well known that fatty acid esters, especially methyl esters and triglycerides, can be used to make amidoamines and imidazolines in place of fatty acids and thus the method of making the emulsifier should not be considered limited to direct acid/amine reaction products. The fatty acid residue is suitably derived from a saturated or unsaturated C<sub>12</sub>-C<sub>22</sub> fatty acid or a mixture of fatty acids, at least 75% of which are C<sub>12</sub>-C<sub>22</sub> fatty acids. Preferably the fatty acid moiety is a saturated or unsaturated mixture at least 75% of which is C<sub>14</sub>-C<sub>22</sub>, more preferably C<sub>14-16</sub>. Preferred fatty acid moieties are obtained from tall oil fatty acid (TOFA), tallow fatty acid, porcine fatty acid, palm oil fatty acid, canola oil fatty acid or rapeseed oil fatty acid, or the triglycerides or methyl esters thereof. The presence of minor amounts of imidazoline does not materially change the performance of the emulsifier, in fact reaction products which are predominantly imidazoline are useful as emulsifiers in the invention.

It has been discovered that a number of parameters may influence the performance of the emulsifier in rigorous tests such as VIM-65. Desireably, the level of emulsifier used should only be as high as necessary to give a storage stable emulsion and the asphalt residue content should be as high as possible, as indicated by passing the sieve test. It is also believed that very small asphalt droplets should be minimized as they may stabilize the emulsion excessively. The amidoamine and/or imidazoline emulsifiers of this invention allow an effective emulsion to be easily made.

The emulsifier may suitably be included in the emulsion in an amount of about 0.75% by weight or less, preferably about 0.5% or less. For chip seal applications generally, it is recommended that the emulsion contain about 65-80% asphalt residue and 0.1-0.5% of the emulsifier. The emulsifier may be prepared at a mole ratio of fatty acid to ethylenepolyamine of 1:1 to 1:1.5, or even higher, and may include both monoacid and diacid adducts. The Saybolt-Furol viscosity is suitably 100 sec. or greater, preferably 200-300 sec. Preferred formulations contain about 68-75% asphalt residue and 0.15-0.35% of the emulsifier and have a pH of between 2.5 and 3.0.

To prepare the emulsion the emulsifier is suitably dissolved or dispersed in water by neutralizing with a mineral acid, suitably at a temperature of about 140° to 150°F (60-66°C), to form an emulsifier solution or mixture such that at least most of the emulsifier is dissolved in water. Hydrochloric acid is the preferred mineral acid. The mineral acid is added in an amount to provide an acidic emulsifier solution, preferably with a pH range of 2.5-3.0.

To form the emulsion, the asphalt residue is added gradually while hot (typically about 280°F (138°C) or higher) to the emulsifier solution in a high shear blender. Typically this is done with continuous flow of both liquids through a continuous colloid/emulsion mill. The mixture is blended at a speed and time which produce a small particle size. Typically the majority of the emulsion is in the range of about 10 micrometer to about 60 micrometer average diameter on a weight basis.

Examples of modifying polymers which may be included in the asphalt residue include, but are not limited to, styrene butadiene styrene block copolymer

(SBS), styrene isoprene styrene block copolymer (SIS), ethylene vinyl acetate copolymer (EVA), ethylene methacrylic acid copolymer (EMA), ethylene acrylic acid copolymer (EAA), or a combination of two or more of these compounds.

Break control agents will not usually be needed or desirable in the compositions of the invention. However, it should be understood that minor amounts of conventional break control agents could be used in the inventive formulations to fine tune the break times for specialized applications. Viscosity control agents such as  $\text{CaCl}_2$  or  $\text{NaCl}$  also may be used in the inventive formulations in some cases.

The formulations of the invention are preferably used in road repair applications such as chip seal applications and spray seal applications such as described in US Patent Nos. 5,474,607 and 5,518,538. Upon contact with stone, per the VIM-65 test, preferred emulsions without break control agents will usually break to a large extent in 30 seconds or less in order to achieve high area % coating on the stone after the water wash. Despite this extremely short break time the preferred emulsions are storage stable for at least one week as determined by passing the sieve test.

More broadly than the VIM-65 test there is a need for faster breaking chip seal emulsions for road repair applications in colder regions or areas subject to impromptu rain showers. The fast breaking chip emulsions are also attractive for roofing applications commonly done with hot tar thereby eliminating the safety and environmental disadvantages of hot tar. Similarly the emulsions can be spray applied as fast setting asphalt coatings, for instance on concrete pipe or on automobile underbodies with lower safety or environmental concerns

than hot applied or solvent-based asphalt coating systems.

The invention is illustrated by the following non-limiting examples.

5

EXAMPLE 1 (Comparative Example)

Asphalt emulsions meeting ASTM D 2397 standards for cationic rapid set emulsion CRS-2 were prepared using the emulsifiers commonly used for chip seal or slurry seal applications and amounts set out in Table 1.

10

Use level and Asphalt residue are the respective weight percentages of emulsifier (100% active) and asphalt in the final emulsion.

5

The emulsifiers were added as emulsifier solutions in water (solution pH 2.5-3.0 adjusted with HCl) to a Charlotte G5 colloidal emulsion mill. Hot AC10 asphalt at 280-300°F (138-149°C) was then pumped to the mill concurrently with the emulsifier solution and blended at high shear to produce emulsions having an approximate particle size distribution of: 20% <1 micrometer ( $\mu\text{m}$ ); 30% 1 to 5  $\mu\text{m}$ ; 20% 5 to 10  $\mu\text{m}$ ; 15% 10 to 20  $\mu\text{m}$ ; 10% 20 to 30  $\mu\text{m}$ ; 5% 30 to 50  $\mu\text{m}$ ; and a small amount larger than 50  $\mu\text{m}$ .

10

The emulsions were tested in accordance with VIM-65 and the stones coated thereby inspected for coating effectiveness. The coating %, estimated by inspection, was recorded and is also reported in Table 1.

To quantify the amount of asphalt that was washed away, that is the portion of the emulsion that had not broken or set in the 30 second mixing, the wash water was extracted with toluene and the extractant evaporated to give its asphalt content. The results are also given in Table 1.

Table 1 Evaluation of conventional chip seal/slurry seal emulsifiers

Emulsifier	Use level wt% of final emulsion	Asphalt residue in final emulsion	VIM-65 test result, area % of aggregate coated with asphalt	wt% of asphalt washed off during VIM-65 test
Redicote 4868	.38%	72%	5 to 10%	87%
Westvaco MQK	.25%	71%	20-30%	79%
Tallow Diamine	.25%	71%	60%	65%
Blend of 50% tallow diamine, 5% tallow primary amine 15% tallow amine propoxylate	.25%	70%	55%	71%

While these emulsions passed the sieve test for storage stability they are clearly not satisfactory in terms of speed of set as measured by the VIM-65 test.

#### EXAMPLE 2 (TOFA-DETA Emulsifiers)

Tall oil fatty acid-diethylenetriamine (TOFA-DETA) amidoamines containing a significant amount of monoamidoamine were then prepared at different ratios of TOFA:DETA as indicated in Table 2. The emulsifiers had a residual acid value of 4.2. The ratio of monoamidoamine to diamidoamine (Mono/Di), as measured by NMR was in the range of 1.8-2.2.



Table 2	
Emulsifier	TOFA:DETA ratio
A	1:1.1
B	1:1.2
C	1:1.3
D	1:1.15

5  
10 Additionally, emulsifiers designated E and F were prepared by post addition of TOFA to Emulsifier B to provide acid values of 6.5 and 8.5, respectively. An emulsifier designated G was prepared by post addition of TOFA to Emulsifier C in an amount to provide an acid  
5 value of 8.5.

#### EXAMPLE 3 (Asphalt Emulsion Formulations of Invention)

The amidoamine emulsifiers prepared in Example 2 were used to prepare emulsifier solutions with mineral acid (HCl) and water at 140-145°F (60-63°C). The mineral  
0 acid was added in intervals and the pH noted. In all cases the mineral acid was added until a stable emulsifier solution pH of 2.5 - 3.0 was obtained. The emulsifier solutions were mixed for at least 15 minutes  
(20-25 minutes for the Emulsifier A solution) to assure  
complete or maximum dissolution of the emulsifier.

Asphalt emulsions were prepared from the various emulsifier solutions using varying amounts of AC10 asphalt residue and varying use levels as shown in Table 3. The emulsions were prepared using a Charlotte G5 colloid mill in the manner described in Example 1.

The emulsions were tested in accordance with VIM-65 and the stones coated thereby inspected for

coating effectiveness. The coating %, estimated by inspection, was recorded and is reported in Table 3.

Table 3				
Example	Emulsifier	Use Level (%)	Asphalt residue (%)	VIM-65 Coating %
3-1	A	0.20	66.4	90
3-2	A	0.20	68.9	95
3-3	A	0.20	71.6	99
3-4	A	0.20	72.5	100
3-5	A	0.30	68.8	97
3-6	A	0.30	71.6	99
3-7	A	0.30	65.7	80
3-8	A	0.30	70.7	92
3-9	B	0.25	68.4	99
3-10	B	0.25	68.6	99
3-11	B	0.25	71.4	99
3-12	C	0.25	69.2	97
3-13	C	0.25	71.4	98
3-14	C	0.20	67.5	96
3-15	C	0.20	69.1	95
3-16	E	0.25	67.6	98
3-17	E	0.25	70.6	99
3-18	F	0.30	67.0	97
3-19	F	0.30	70.2	97
3-20	G	0.20	67.7	97
3-21	G	0.20	70.0	99
3-22	G	0.30	67.4	99
3-23	G	0.30	70.2	99

3-24	D	0.25	71.7	100
3-25	D	0.25	72.3	100

The coating % results show that the TOFA-DETA emulsifier gives exceptionally good performance, which can be optimized by careful adjustment of asphalt residue amounts, emulsifier use levels and emulsifier use levels. The Examples 3-24 and 3-25 fully met the requirements of VIM-65 without emulsion destabilizing ingredients. The emulsions above all passed the sieve test for storage stability.

#### EXAMPLE 4 (Asphalt Emulsion Formulations of Invention)

In the manner of Example 1 TOFA-DETA emulsifiers were tested at various use levels for both % coating under the VIM-65 test and for % asphalt washed off during the VIM-65 test. AC10 asphalt was used except for Examples 4-1 and 4-6, where a 60/40 weight basis blend of AC20 and AC5 asphalt was used to approximate the characteristics of AC10 asphalt. Results are given in Table 4.

Table 4 Results with TOFA DETA amidoamines

Example	Emulsifier	Use level %	Asphalt residue (%)	VIM-65 Coating %	VIM-65 % Asphalt washed off
4-1	A	.25	70	85	54
4-2	A	.2	71	100	
4-3	D	.125	70	95	42
4-4	D	.25	71	100	46

4-5	D	.5	70	55	67
4-6	D	.25	71	95	40

## EXAMPLE 5

Further evaluations were done with amidoamines made by standard synthetic methods using various fatty acids and with various ethylene amines using the same methods as in the previous examples. The results are shown in Table 5

Table 5

Example	Fatty Acid	Amine	Acid: amine ratio	Asphalt
5-1	TOFA	Ethylene diamine	1:1.1	AC 10
5-2	TOFA	TETA	1:1.1	AC 10
5-3	TOFA	TETA	1:1.1	AC20/AC5**
5-4	TOFA	TEPA	1:1.1	AC20
5-5	TALLOW	DETA	1:1.1	AC20
5-6	RAPESEED	DETA	1:1.1	AC20
5-7	LAURIC	DETA	1:1.1	AC20

\*\* 60/40 Wt % blend.

Example	Use level %	asphalt residue	VIM-65 coating %	VIM-65 Asphalt washed off %
5-1	.25*	69	98	46
5-2	.25	69	100	41
5-3	.25	70	90	63
5-4	.25	69	100	41
5-5	.25*	70	100	37

5-6	.25	70	100	33
5-7	.25	71%	100	-10***

\* Added as 0.35 wt % of a 70% solution in Isopropyl alcohol.

\*\* 60/40 Wt % blend.

\*\*\*Emulsion failed sieve test with 0.8% on the screen.

Attempts to emulsify asphalt with DETA amidoamines made from caprylic (octanoic) acid were unsuccessful.

#### EXAMPLE 6

To explore the effect of monoacid versus diacid residue content and the effect of imidazoline versus amidoamine content, several different emulsifiers were made from TOFA and DETA using various ratios of TOFA and DETA. The imidazoline content was controlled by conventional techniques. The emulsifiers were analyzed by NMR. The emulsifiers are described in Table 6 where ratios and percentages are given on a mole basis. In Table 6, "monoalkyl imidazoline" refers to the imidazoline adduct formed from one mole of fatty acid per mole of DETA and "dialkylimidazoline" refers to the adduct of two moles of fatty acid per mole of DETA.

Table 6

Example	TOFA:DETA ratio	Mono amidoamine (%)	Diamidoamine (%)	Monoalkyl imidazoline	Dialkyl imidazoline	DETA %
6-1	1:1.2	49	41			9
6-2*		10	8	44	35	2
6-3	2:1	12	62	3	22	

6-4	1:5	37	5	11	46	
6-5	1:1.1			45	55	

\* Sample 6-2 is a commercial TOFA-DETA imidazoline emulsifier.

5

Emulsions were prepared and tested as in the previous examples at an emulsifier use level of 0.225 wt%. Except as indicated in Table 7, the emulsions were prepared from AC-10 asphalt. All of the emulsions passed the sieve test. Results are given in Table 7.

10

Table 7

Emulsifier	Residue Wt %	Mix time (sec)	VIM-65 Coating %	VIM-65 % Asphalt washed off
6-1	72	25	100	55
6-2	71*	30	95	42
6-3	72	25	100	49
6-4	72	20	100	
6-5	72	25	100	44

\*Blended AC20 and AC5 asphalt

15

20

The foregoing example demonstrates that the emulsifier made from TOFA and DETA is effective in achieving good coating of aggregate as evidenced by the VIM test over a wide range of the amidoamine/imidazoline ratios and mono to di acid ratios.

5

The above examples and disclosure are intended to be illustrative and not exhaustive. These examples and description will suggest many variations and alternatives to one of ordinary skill in this art. All these alternatives and variations are intended to be included within the scope of the attached claims. Those

0

familiar with the art may recognize other equivalents to the specific embodiments described herein which equivalents are also intended to be encompassed by the claims attached hereto.

5

## CLAIMS

1. A surface repair or finishing method comprising  
applying an aqueous asphalt residue emulsion onto a  
substrate surface;  
5           applying stone aggregate to the emulsion after  
the emulsion has been applied to the surface,  
wherein the stone aggregate comprises no more than 10% by  
weight of material of less than 16 mesh USS size, and the  
emulsion comprises a fatty acid/ethylenepolyamine  
10       emulsifier characterized by at least one fatty acid  
residue and an ethylenepolyamine residue, the at least  
one fatty acid residue and the ethylenepolyamine residue  
together forming an amidoamine compound or an imidazoline  
compound or a mixture thereof.  
15
2. A method as in claim 1 wherein the substrate is a  
road.
3. A method as in claim 2 wherein the emulsion is  
10       applied by spraying.
4. A method as in claim 1 wherein the substrate is a  
roof.
- 5       5. A method as in claim 1 wherein the fatty acid residue  
of said emulsifier is a residue of a saturated or  
unsaturated C<sub>12</sub>-C<sub>22</sub> fatty acid or a mixture of fatty acids,  
at least 75% of which are C<sub>12</sub>-C<sub>22</sub> fatty acids.
- 0       6. A method as in claim 5 wherein said fatty acid  
residue is a residue of a saturated or unsaturated fatty  
acid mixture at least 75% of which is C<sub>14</sub>-C<sub>22</sub>.



7. A method as in claim 5 wherein at least 75% of said fatty acid mixture is C<sub>14</sub>-C<sub>18</sub> fatty acid.

5 8. A method as in claim 1 wherein said fatty acid residue is derived from a member of the group comprising tall oil fatty acid, tallow fatty acid, porcine fatty acid, palm oil fatty acid, cannola oil fatty acid, rapeseed oil fatty acid, and the triglycerides and methyl esters thereof.

0 9. A method as in claim 1 wherein the ethylenepolyamine residue of said emulsifier is the residue of a member of the group consisting of ethylenediamine, diethylenetriamine, triethylenetetraamine,  
5 tetraethylenepentaamine and mixtures thereof.

10. A method as in claim 1 wherein the fatty acid residue is tall oil fatty acid residue and the ethylenepolyamine residue is diethylenetriamine residue.

11. A method as in claim 1 wherein the emulsion, when tested in accordance with VIM-65 provides about 90% or more coverage of the test stone.

12. A road repair method as in claim 11 wherein said coverage is 100%.

13. A method as in claim 1 wherein the emulsifier is present in the emulsion in an amount of no more than 0.75% by weight.

14. A method as in claim 1 wherein substantially all of the aggregate is sized at greater than 16 mesh USS.

15. A method as in claim 1 wherein the emulsion has an asphalt content of about 65% by weight or more.
- 5 16. A method as in claim 1 wherein the emulsion has an asphalt content of about 68% by weight or more.
- 10 17. A method as in claim 1 wherein not more than 0.1% of the emulsion is captured on a 20 mesh USS sieve, after one week storage of the emulsion.
- 15 18. A surface repair or finishing method comprising spray applying an aqueous asphalt residue emulsion onto a substrate surface, wherein the emulsion comprises an asphalt residue content of at least 65%, and a fatty acid/ethylenepolyamine emulsifier characterized by at least one fatty acid residue and an ethylenepolyamine residue, the at least one fatty acid residue and the ethylenepolyamine residue together forming an amidoamine compound or an imidazoline compound or a mixture thereof.
- 0 19. A method as in claim 18 wherein not more than 0.1% of the emulsion is captured on a 20 mesh USS sieve, after one week storage of the emulsion.
- 5 20. A method as in claim 18 further comprising subsequently applying stone aggregate to the emulsion after the emulsion has been applied to the surface.
21. A method as in claim 18 wherein the substrate is made of concrete.
22. A method as in claim 21 wherein the substrate is a concrete pipe segment.

23. A method as in claim 18 wherein the substrate is an automobile underbody.

24. A method as in claim 18 wherein said fatty acid residue is a residue of a saturated or unsaturated  $C_{12}$ - $C_{22}$  fatty acid or a mixture of fatty acids, at least 75% of which are  $C_{12}$ - $C_{22}$  fatty acids.

25. A method as in claim 24 wherein said ethylenepolyamine residue is diethylenetriamine residue.

26. A method as in claim 18 wherein the emulsifier is present in the emulsion in an amount of no more than 0.75% by weight.

27. A method as in claim 26 wherein the emulsifier is present in the emulsion in an amount of no more than 0.5% by weight and said asphalt residue is present in the emulsion in an amount of at least 68% by weight.

28. An aqueous asphalt emulsion composition comprising on a composition weight basis:

65-80% asphalt residue; and

0.10-0.5% of a fatty acid/ethylenepolyamine emulsifier characterized by at least one fatty acid residue and an ethylenepolyamine residue, the at least one fatty acid residue and the ethylenepolyamine residue together forming an amidoamine compound or an imidazoline compound or a mixture thereof.

29. A composition as in claim 28 wherein the asphalt residue is 68-75% of the composition.

30. A composition as in claim 28 wherein the emulsifier is 0.15-0.35% of the composition.

31. A composition as in claim 28 having a pH of 2.5-3.0.

32. A composition as in claim 28 wherein said fatty acid residue is a residue of a saturated or unsaturated  $C_{12}$ - $C_{22}$  fatty acid or a mixture of fatty acids, at least 75% of which are  $C_{12}$ - $C_{22}$  fatty acids.

33. A composition as in claim 28 wherein said fatty acid residue is derived from a member of the group comprising tall oil fatty acid, tallow fatty acid, porcine fatty acid, palm oil fatty acid, canola oil fatty acid, rapeseed oil fatty acid, and the triglycerides and methyl esters thereof.

34. A composition as in claim 28 wherein the ethylenepolyamine residue of said emulsifier is the residue of a member of the group consisting of ethylenediamine, diethylenetriamine, triethylenetetraamine, tetraethylenepentaamine and mixtures thereof.

35. A composition as in claim 28 wherein the fatty acid residue is tall oil fatty acid residue and the ethylenepolyamine residue is diethylenetriamine residue.

36. A composition as in claim 28 wherein the emulsifier is prepared at a mole ratio of fatty acid to diethylenetriamine of from about 1:1.1 to about 1:1.5.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/12568

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(7) : C09D 195/00 US CL : 106/277 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 106/277  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) NONE		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X  ----- Y	US 3,096,292 A [MERTENS] 02 July 1963, see entire document.	28-30, 32-36 ----- 1-27, 31
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* *A* *E* *L* *O* *P*	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	*T* *X* *Y* *G* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
Date of the actual completion of the international search 29 JULY 2000		Date of mailing of the international search report 11 AUG 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer <i>David M. Brunzman</i> DAVID M. BRUNSMAN Telephone No. (703) 308-0661